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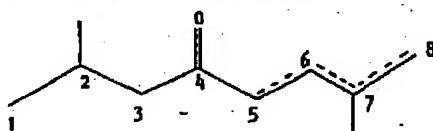
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(54) Perfumery compounds and their preparation.

(57) Useful perfumery compounds have the formula



where there is a double bond in one of the 5,6 or 6,7 or 7,8 positions. The compounds may be made by reaction of 2-methyl-pentan-4-one with isobutyraldehyde followed by dehydration, preferably in the presence of a weak acid.

BUSH BOAKE ALLEN LIMITED

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## PERFUMERY COMPOUNDS AND THEIR PREPARATION

The great majority of synthetic perfumery compounds have a terpenoid or other cyclic structure and there are  
5 relatively few synthetic perfumery compounds having a substantially linear structure.

If a compound is to serve as a synthetic perfumery compound it has to comply with three essential requirements and failure of either requirement will  
10 prevent it being a useful synthetic perfumery compound. One requirement is that the compound has, at low concentrations, a pleasant odour and can be blended with other perfumery compounds to give pleasant blended odours. Another is that it is stable in compositions in  
15 which it can be used, for instance when used in, e.g., soap or shampoo its odour and other properties must not change on storage. The other requirement is that the compound must be capable of being synthesised at low cost from readily available starting materials. There is  
20 little or no commercial interest in compounds as synthetic perfumery compounds if their synthesis requires expensive and poorly available starting materials or if it requires expensive process steps, since the reason for providing synthetic perfumery compounds is to get away  
25 from the expense of natural perfumery compositions.

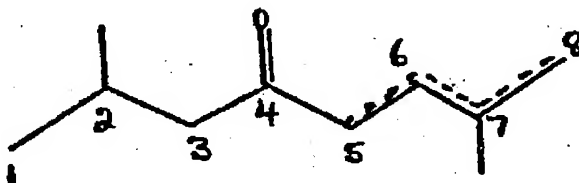
Most of the thousands or millions of low molecular weight aliphatic compounds have an odour but, despite this, very few of them are useful as synthetic perfumes since very few have the required combination of useful  
30 odour characteristics (especially when blended), stability to compositions in which they can be used (e.g., soaps), and low cost.

A few compounds having a chain of 8 carbon atoms are known to have pleasant odours, for instance as disclosed  
35 in "Perfume and Flavour Materials", Volumes I and II, by

5. Arctander (published 1969). One such compound is generally known as dimethylocteneone and in particular is 4,7-dimethyloct-6-ene-3-one (CAS No: 2550-11-0). However this compound is very costly to make and has a green, geranium, oily odour.

Another octeneone compound is 2,6-dimethyl-octa-5,7-diene-4-one. This occurs naturally in tagetes but is not available commercially. It is known to have an odour but it has not previously been proposed as contributing useful odour properties to perfumery compositions and, in particular, it has been very expensive and difficult to make. Accordingly it has not been adopted as a commercially useful synthetic perfumery compound.

The compounds of the invention are the compounds of Formula 1



where there is a double bond in one of the 5,6 or 6,7 or 7,8 positions. This invention includes the individual compounds and mixtures of two or all three of these compounds. The preferred compound of Formula 1 has the double bond in the 5,6 position and is 2,7-dimethyl-oct-5-ene-4-one (alternatively known as 2,7-dimethyl-oct-3-ene-5-one).

The 5-ene compound may be obtained free of the other two compounds or blended with either or both of the other two compounds. Preferred blends of the invention contain at least 20%, preferably at least 50% and most preferably at least 75% by weight of the 5-ene compound with the balance preferably being the 6-ene compound or,

less preferably, a mixture of the 6-ene compound with a small amount, typically 1 part in 6, of the 7-ene compound.

5 The compounds of the invention, and especially blends consisting of or mainly comprising the 5-ene compound, are of particular value as synthetic perfumery compounds because of the combination of perfumery properties and ease of synthesis.

10 A perfumery composition according to the invention comprises one of the novel compounds, preferably the compound of Formula 1. The composition generally contains at least one other odiferous chemical. The composition generally comprises a large number of odiferous chemicals.

15 The composition may be provided as a concentrate for incorporating in a consumer composition or may be provided as a consumer composition. The composition can be one of a wide variety of consumer compositions, but preferably take the form of a cologne, cream, lotion, 20 soap, detergent, air freshener or antiperspirant. Particularly preferred compositions are colognes and especially, air fresheners, for instance aerosol air fresheners.

25 The compounds of the invention, and especially the 5-ene compound, have a very strong odour having fruity, taget and chamomile characteristics. It is of particular value for contributing a natural jasmine odour and, especially of imparting a natural note to Bergamot and lemon fragrances.

30 The compounds, and especially the 5-ene compound, are of suitable stability for most perfumery uses, but the compositions in which they are formulated are preferably not highly alkaline or highly acidic. Preferably the compositions have pH between 3 and 10, 35 generally between 5 and 8.

The compounds of Formula 1 may be made by reacting 2-methyl-pentan-4-one with isobutyraldehyde and dehydrating the product.

The process may be conducted in the presence of a mixed solvent such as aqueous dioxane (in the presence of alkali) but preferably is conducted as a heterogeneous mixture of aqueous alkali, ketone and aldehyde. To promote transfer between the phases the reaction is preferably conducted in the presence of a phase transfer catalyst. A suitable catalyst is cetyl trimethyl ammonium bromide but other phase transfer catalysts that may be used include other tetra alkyl quaternary ammonium halides such as tetrabutyl ammonium iodide and tricaprylyl methyl ammonium chloride. The ratio by weight of the ketone to the aldehyde is typically in the range 1:4 to 10:1, preferably 5:1 to 2:1 and most preferably 3:1 to 4.5:1. The amount of water in the mixture is generally from 0.1 to 2 parts, most preferably about 0.3 to 0.8 parts, by weight per part by weight organic components in the mixture. The alkali is preferably sodium hydroxide. The amount of phase transfer catalyst agent is generally in the range 0.01 to 1%, preferably 0.05 to 0.5%, by weight of the reaction mixture.

The reaction mixture is generally formed by adding the aldehyde to a preformed mixture of the other components. Reaction is generally conducted at 50 to 95°C, preferably 75 to 85°C, over a period of 1 to 6 hours, generally 3 to 4 hours.

This reaction results in the production of a saturated intermediate, 2,7-dimethyl-oct-6-hydroxy-4-one. The saturated intermediate must then be dehydrated to form the compound or compounds of Formula 1. Dehydration can be conducted on the saturated compound after isolation from the reaction mixture, for instance

by decanting off the aqueous layer and washing the organic layer, containing the saturated compound, free of alkali with water, but generally it is satisfactory and is preferred to conduct the dehydration on the reaction mixture without isolation of the saturated intermediate.

Dehydration can be effected by distilling in the presence of a dehydrating agent such as paratoluene-sulphonic acid. However, we find that the use of a strong acid promotes the formation of the 6-ene and/or 7-ene compounds and that improved yield of the 5-ene compound is achieved with weaker acids. Suitable acids that are weaker than paratoluene sulphonic acid and which are useful in the invention include aliphatic carboxylic acids, typically saturated aliphatic acids containing up to 6 carbon atoms, and most preferably aliphatic dicarboxylic acids, oxalic acid and maleic acid being particularly preferred. The acid preferably has a dissociation constant of from 1 to 2.5.

The preferred way of dehydrating is to heat the reaction mixture under reflux in the presence of the selected acid. The amount of acid is often in the range 0.1 to 5% (by weight based on the weight of saturated intermediate) with amounts of 0.5 to 5% being particularly preferred when using oxalic acid and other saturated aliphatic acids.

The distillation is preferably effected by heating the reaction mixture under reflux, generally at atmospheric pressure, for instance for from 4 to 8 hours and azeotropically removing the water.

The following are examples of the invention.

EXAMPLE 1

To a mixture of methyl isobutyl ketone (1014 gms) water (690 mls) sodium hydroxide pellets (7 gms) and cetyltrimethylammonium bromide (3.6 gms) stirred at 80°C is added isobutyraldehyde (480 gms) over a period of one

hour. After the addition is complete, the reaction is stirred at 80°C for a further four hours. The stirring is then stopped and the aqueous layer is decanted off and rejected. The organic layer containing the desired  
5 intermediate is then washed free of alkali with water.

Oxalic acid (9 gms) is then added to washed product containing the intermediate and the mixture is refluxed, removing the water formed via a Dean and Stark head. When no more water is obtained, the mixture is cooled and  
10 washed free of acid with aqueous sodium carbonate solution.

Fractionation of the product yields ca. 400 gms of a product having a boiling point 69°C at 5 torr. Analysis by gas liquid chromatography indicates a composition of  
15 80% dimethyloct-5-enone and 20% dimethyloct-6-enone.

#### EXAMPLE 2

Repeating Example 1 by heating (in the dehydration step) with 2 gms of p-toluene sulphonic acid for 14 hours yields a product whose composition is 23%  
20 dimethyloct-5-enone, 66% dimethyloct-6-enone and 11% dimethyloct-7-enone. The odour properties of this mixture are less effective and useful than those of the mixture of Example 1.

#### EXAMPLE 3

25 A perfumery concentrate is formulated in conventional manner from

Musk ketone	0.23
Dipropylene Glycol	0.57
Citral pure	0.75
30 Hedione	0.60
Cis 3 hexenyl salicylate	0.08
Ethoxy hexoxy ethane (lilivert)	1.50
Mandarin aldehyde 10	0.02
Neroli Synth. BB40	1.28
35 Orange oil sweet Florida	24.06

	Osyrol	4.51
	Patchouli oil Iron free	0.23
	Ros mary oil Spanish	0.60
	Spearmint oil American	0.15
5	Thyme oil White Rect.	0.23
	Vertofix Cobur	0.53
	Bergamont Synth. 6749	63.16
	Blend of Example 1	1.50
10		<hr/> 100.00 <hr/>

The process of Example 1 is a very simple process to  
operate and gives a high yield of the defined blend at  
15 relatively low cost. The perfumery properties of the  
concentrate of Example 3, and of other compositions  
containing the 5-ene compound of Formula 1 are very  
desirable. These concentrates can be used in the  
preparation of consumer compositions of the types  
20 discussed above.

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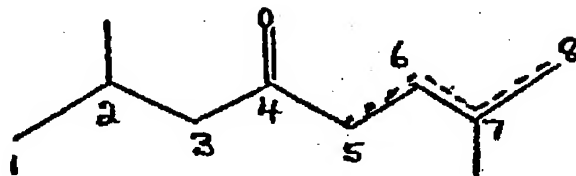
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CLAIMS

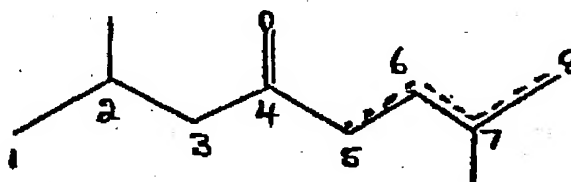
1. A dimethyl oct none compound characterised in that it has the formula



10 where there is a double bond in one only of the 5,6 and 6,7 and 7,8 positions.

2. A compound according to claim 1 in which the double bond is in the 5,6 position.

3. A blend of compounds of the formula



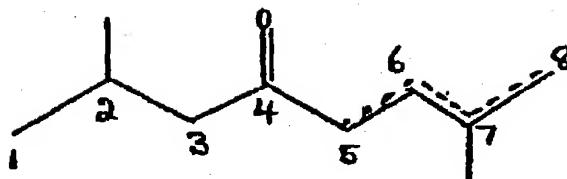
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where there is a double bond in one only of the 5,6 and 6,7 and 7,8 positions and in which at least 20% by weight of the blend is the compound in which the double bond is in the 5,6 position.

25 4. A blend according to claim 3 in which at least 50%, and preferably at least 75%, by weight of the blend is the compound in which the double bond is in the 5,6 position.

5. A perfumery composition comprising a  
30 dimethylocteneone compound and at least one other odiferous chemical characterised in that the dimethylocteneone compound is a compound according to claim 1 or claim 2 or a blend according to claim 3 or claim 4.

35 6. A method of making a compound of the formula



- 5
- comprising reacting 2-methyl-pentan-4-one with isobutyraldehyde and dehydrating the resulting saturated product.
- 10 7. A method according to claim 6 in which the reaction of 2-methyl-pentan-4-one with isobutyraldehyde is conducted in a heterogeneous reaction mixture comprising the aldehyde, the ketone, aqueous alkali and a phase transfer catalyst.
- 15 8. A method according to claim 6 or claim 7 characterised in that the dehydration is conducted by distilling the resulting saturated product, or the reaction mixture containing it, in the presence of an aliphatic carboxylic acid.
- 20 9. A method according to claim 6 comprising reacting the aldehyde with the ketone in a heterogeneous mixture comprising aqueous alkali and a phase transfer catalyst and dehydrating the resultant saturated product by refluxing the product, or the reaction mixture containing
- 25 it, in the presence of oxalic acid.
- 30
- 35